3. DISCUSSION

3.1 Test Plan Objectives

This series of tests had the following six objectives, as described in the Test Plan for Nitrate Explosives Tests (INEEL 2000).

1.   Severity—to determine upper bounds on the severity of explosive events and on the rates of deflagrative processes in actual operations

2.   Critical temperature—to determine the temperature at which explosive or reactive events occur

3.   Migration of oils—to determine whether oils will migrate from the heated zone or remain in sufficient quantities to undergo violent reaction

4.   Explosion vs. burning—to determine whether nitrate and organic materials, mixed more uniformly than expected in the actual waste deposits, will undergo explosion or rapid burn when subjected to heat

5.   Mixing effects—to determine the degree of mixing required for explosion, whether the intimate mixtures do explode

6.   Burning propagation—to determine the burn propagation rates or the intensity of nitrate and organic reactions for such mixtures, if they do occur.

All of the test program objectives were achieved and are addressed individually in the following discussion.

3.2 Test Schedule Phases

The tests described in this report were carried out in four phases to pursue an iterative (or observational) approach, and also to provide the appropriate flow of funding for the investigation. Thus, if the results from the first phase had indicated no severe reactivity of the nitrates, the follow-on phases would have been unnecessary. In fact, each phase identified more data gaps, and the project progressed to acquire the necessary data.

3.2.1 Phase 1

This phase consisted of the Henkins, Koenen, burn-rate determinations (labeled as Test 12), and initial 5-gal tests (labeled as Tests 1 through 4) (see Sections 2.1, 2.2, 2.3, and 2.4, respectively). The reactivity of the nitrates with charcoal and cellulose in the 5-gal tests led to the decision to perform Phase 2.

3.2.2 Phase 2

This series of tests was performed in 55-gal drums to scale up the reactions observed in Phase 1. This phase involved Tests 13, 17, 21, and 23. The reactivity observed in Test 21 with nitrates and pyrolyzed rags led to the decision to bury the drum beneath 3 m (10 ft) of overburden for Test 23. The disruption of the surface by the full drum in Test 23 led to the decision to perform further tests in Phase 4.

3.2.3 Phase 3

The reactivity observed in Phases 1 and 2 led to the expansion of 5-gal testing performed in Phase 3. To test more "realistic" conditions, nitrates were placed in contact with (rather than mixed with) rags, pyrolyzed rags, and graphite. Funding was also provided for additional 55-gal testing, should it prove necessary. The objectives of the test plan were completed in Phases 1, 2, and 3. The first NMT report, issued in FY 2000, was based on Phases 1, 2, and 3 (EMRTC 2000). The second NMT report, based on Phase 4, was issued in FY 2001 (EMRTC 2001). This INEEL report is based on both of the NMT reports.

3.2.4 Phase 4

Breaching the surface observed in Test 23 (see Section 2.5.2.4), with a 3-m (10-ft) sand overburden, led to the decision to perform the mitigation tests in Phase 4. It was decided to change the shape of the burial area to avoid the gun-barrel effect of the narrow hole. It was further decided to limit the materials to only that which could be obtained by pyrolyzing one full drum of rags, rather than a full drum of pyrolyzed rags and nitrate salts. A full drum was used in Test 23 to determine boundary conditions. A more realistic quantity was used in Phase 4 to determine mitigation effectiveness. Funding was available because of the cost reductions achieved in Phase 3 and by careful planning based on the results. A separate report was issued by EMRTC for the work performed during FY 2001 (EMRTC 2001).

3.3 Nitrate Reactions

3.3.1.1 Alkali metal nitrates, in this case KNO_3 and $NaNO_3$, are not explosive per se, but are capable of explosive reactions with a fuel. Ammonium nitrate (NH_4NO_3), in contrast, is inherently unstable. When supplied with suitable activation energy, NH_4NO_3 can self react according to the following equations.

$$NH_4NO_3 \rightarrow N_2 + 2H_2O + \tfrac{1}{2}O_2 \tag{1}$$

or

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \tag{2}$$

or

$$8NH_4NO_3 \rightarrow 5N_2 + 4NO + 2NO_2 + 16H_2O \tag{3}$$

Urbanski (1965) presented ΔH values of -346.5, -133.6, and -132.6 kcal/kg for the above reactions using ΔH_f for $NH_4NO_3 = -88.6$ kcal/mole.

Ammonium nitrate (NH_4NO_3) has excess oxygen and its explosive power is enhanced by the addition of fuels such as powdered aluminum, or hydrocarbons such as kerosene or diesel fuel.

If fuel is added, N_2O does not form as a product. Instead, M_xO_y are formed, in addition to more H_2O along with the CO_2, contributing to the exothermicity of the reaction.

Neither KNO_3 nor $NaNO_3$, on the other hand, has hydrogen (or carbon) built into the molecule, and must be supplied with fuel to react (see Equation (4)). A source of either (or both) hydrogen and carbon could supply the necessary fuel.

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$$74KNO_3 + 5C_{12}H_{26} \rightarrow 60CO_2 + 37N_2 + 28H_2O + 74KOH \tag{4}$$
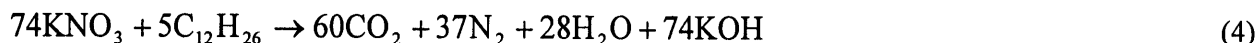
Hence, five dodecanes reduces 74 nitrates.

Using diesel fuel, cetane, or hexadecane as "ideal" diesel fuel (see Equation (5)).

$$98KNO_3 + 5C_{16}H_{34} \rightarrow 80CO_2 + 49N_2 + 36H_2O + 98KOH \tag{5}$$
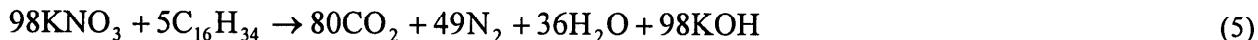
Without fuel, the simple decomposition becomes the following:

$$2KNO_3 \rightarrow K_2O + N_2O_5 \rightarrow K_2O + N_2O + 2O_2 \tag{6}$$

Equation (6) is highly endothermic. In the presence of moisture, the K_2O would react to form $2KOH$, which, with sufficient moisture, would hydrate with the liberation of heat.

With carbon as fuel, a possible reaction becomes Equation (7) or (8).

$$2KNO_3 + 3C \rightarrow 2CO_2 + CO + N_2 + K_2O \tag{7}$$

or

$$2KNO_3 + 3C \rightarrow CO_2 + CO + N_2 + K_2CO_3 \tag{8}$$

The KOH would also react with the CO_2 to form $KHCO_3$ or K_2CO_3 and more heat.

Another reaction presented by Urbanski burns the postulated intermediate CO to CO_2 (see Equation (9)) (Urbanski 1967).

$$4KNO_3 + 5C \rightarrow 3CO_2 + 2N_2 + 2K_2CO_3 \tag{9}$$

Urbanski states that 779 kcal/kg is evolved with a gas volume V_0 of 240 L/kg, and that the calculated temperature is 2700°C.

Davis (1943) presented values obtained by Noble and Abel[c] for RLG black-powder burning, which produced 718.1 cal/gram (or 718.1 kcal/kg) and 271.3 cc of permanent gas measured at 0°C and 760 mm pressure (standard temperature and pressure). They calculated that the explosion of the powder produces a temperature of about 3,880°C.

Equation 10 portrays the reaction of $NaNO_3$ with cellulose.

$$5C_6H_{10}O_5 + 24NaNO_3 \rightarrow 12Na_2CO_3 + 18CO_2 + 25H_2O + 12N_2$$
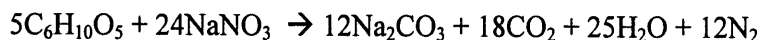
$$5 \times 162.14 + 24 \times 85.00 = 810.70 + 2040 = 2850.70$$

Therefore,

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c. Noble, Andrew, and Abel, *Phil. Trans.*, 1875, 49; 1880, 203; *Mem. poudres*, 193 (1882). See also Debus, *Proc. Roy. Soc.*, 30, 198 (1880).

%cellulose = 810.7/2850.7 = 28.43 and

% nitrate = 2040/2850.7 = 71.57 (10)

Equation (11) shows the reaction of KNO_3 with cellulose.

$$5C_6H_{10}O_5 + 24KNO_3 \rightarrow 12K_2CO_3 + 18CO_2 + 25H_2O + 12N_2$$

$$5 \times 162.14 + 24 \times 100.1 = 810.7 + 2426.4 = 3237.1$$

Therefore,

% cellulose = 810.7/3237.1 = 25.04

% nitrate = (2426.4/3237.1) × 100 = 74.96. (11)

3.4 Oils and Nitrates

The greatest concern leading to this test series was the possibility of an explosive reaction between the nitrate salts present in the SDA (in the form of 745 sludges) and the large amount of oils present as 743 sludges. These oils primarily include Texaco Regal R&O or Shell Vitrea machining oils cut with chlorinated solvents such as CCl_4, PCE, TCE, and TCA. The oils were packaged with calcium silicate to form a solid sludge at the RFP, but after many years in the SDA, they may have separated because of decomposition or being flooded with water. Oils becoming mobile (when heated) and running into ruptured nitrate drums and exploding during ISV constituted the scenario of concern. Nitrates melting and flowing into oil drums, and again possibly exploding when heated, constituted another scenario. Furthermore, the CCl_4 that was postulated to reduce the reactivity of the oils may well have evaporated from the oil and migrated, as evidenced by the large amounts of CCl_4 removed from the SDA by Organic Contamination in the Vadose Zone (OCVZ) extraction methodology.

The ITRP had mixtures of nitrates and 10% Regal oil tested for impact, static, and friction without any initiations. A 1-gal mixture, when boosted with 150 g (0.33 lb) of Pentolite, did explode. However, effects were only estimated by crater size. The EMRTC testers were also unable to cause explosions with mixtures of nitrates and oil. The Henkin and Koenen tests gave no explosions with the oil mixtures, even at the smallest orifice size in the Koenen test. Although the drums were severely oxidized, the 5-gal tests with oil and with oil mixed with equal parts of CCl_4, only caught fire or smoked. The 55-gal test was heated for 1 week at 500°C but did not explode. However, the absence of an event does not prove that one could not take place under any circumstances. At 500°C, the oil distills from the drum with decomposition. It may be possible to find a lower temperature at which the oil would not migrate, but it would eventually react fast enough with the decomposing nitrate salts to explode. The intimate interface of oil-soaked nitrate provides a possible reaction zone. The consequences of such an explosion could be severe, as several hundred pounds could be involved with a nitrate drum into which oil has flowed.

The case of oil and $NaNO_3$ or KNO_3 is similar to ANFO explosives, but in the case of NH_4NO_3, the compound can explode without any oil present. The diesel fuel sensitizes the NH_4NO_3 and adds to the explosive energy, but is not necessary for an explosion.

3.5 Graphite and Nitrates

Graphite did not explode when the drum was heated on either a 5- or a 55-gal scale when nitrate salts in an 80 to 20 wt% ratio were placed on top of the graphite. The intense heat of the fires melted the

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drums. In Test 19, where the graphite and nitrate salts were mixed 100 turns, the reaction was energetic and rapid enough to disrupt the surface. One could argue that the graphite, having a crystalline structure, is at a lower energy state than amorphous carbon, and hence has a lower reaction energy and a higher energy barrier to cross to reach the transition state.

The tests performed represent the worst-case scenarios, as the drums actually present in the SDA contain mostly graphite pieces, and are unlikely to contain all fines or scarfings. Nitrates in contact with graphite, as is the case with oil, provide opportunities for large explosive quantities in one drum.

3.6 Pyrolyzed Rags and Nitrates

Nitrate salts can react with carbon according to the following equation:

$$4KNO_3 + 5C \rightarrow 3CO_2 + 2N_2 + 2K_2CO_3 \tag{12}$$

The RFP waste contains drums of rags and paper. Upon pyrolysis (i.e., heating in the absence of oxygen), the cellulose will lose water to form carbon. Nitrates react explosively with carbon.

Andrew Noble (see Davis [1943]) suggested omitting sulfur in powder mixtures, and found a mixture of 80% KNO_3 and 20% charcoal to be somewhat stronger than black powder of normal composition, which contains 75% KNO_3, 15% charcoal, and 10% sulfur (Urbanski 1967). A stoichiometric mixture contains 87.1% KNO_3 and 12.9% charcoal. Historically, explosives workers may have used excess charcoal because it was more abundant and also less expensive than KNO_3. Also, although the stoichiometry for oxygen balance to CO_2 is 87% KNO_3, a richer mixture will simply produce more CO. There is a fairly broad band of reactant ratios that will produce similar energies. Sodium nitrate ($NaNO_3$) has also been substituted for KNO_3 in "brown blasting powders," which are similarly energetic.

The combinations of nitrates and pyrolyzed rags in these tests exploded consistently. It should be emphasized, however, that no detonations occurred. When the drum was filled with 85.2 kg of nitrate on top of carbon in Test 23, the explosion breached the surface. When more realistic maximum quantities of 67.6 and 69.2 kg of carbonized rags and nitrates were used in Tests 24 and 27, respectively, the surface was not breached. It is clear that this is a narrow margin of safety. Test 23 represents the maximum stoichiometric quantity of nitrates and carbon from pyrolyzed rags that could be packed into a drum. Tests 24 and 27 represent the maximum reactants that can result when the maximum quantity of rags that can be packed into a drum is pyrolyzed, and the stoichiometric quantity of nitrates added. Test 23 had a narrow, gun-barrel-like hole filled with sand. Tests 24 and 27 had holes shaped to meet Occupational Safety and Health Administration slope standards and filled with native dirt with compaction from the drum to grade level.

It should be noted that the ingredients in Tests 23, 24, and 27 were not mixed. The nitrate salts were placed on top of the carbon formed from pyrolyzed rags. The only mixing occurred as the nitrate salts softened and melted. It would be reasonable to infer that the explosive reaction took place only at the interface between the salts and the pyrolyzed rags, and that the reaction was probably incomplete. Nevertheless, a mechanism for more complete mixing during ISV in the SDA is not obvious.

3.7 Nitrate-Soaked Rags

Nitrate-soaked rags exploded in these tests at lower temperatures than the nitrates on top of pyrolyzed rags. The explosive effects were less because only 30 kg (66 lb) of soaked and dried rags could be forced into a 55-gal drum. A drum was ignited with a hot wire and exploded at a temperature of only

150°C. Again, this was a worst-case and highly unlikely scenario. The 65-wt% nitrate ratio was chosen as the highest nitrate concentration that could be achieved by the ITRP in their tests. During testing, this concentration could only be achieved by soaking the rags in a saturated nitrate solution at 60°C. The stoichiometric ratio for burning to CO_2 would be closer to a 73% nitrate ratio. It should be noted, however, that the 52% nitrate-soaked rags in Test 12d burned 25% faster than the 63% nitrate-soaked rags in Test 12c. Cheetah computer code (LLNL 1998) calculations indicate a rather broad range over which the soaked rags can burn or deflagrate. It is not difficult to construct a scenario in which nitrate salts are dissolved from drums in the SDA and transported in solution to rag-filled drums. It is difficult to then have the wet rags dried to such a concentration of the nitrates underground.

3.8   Nitrates and Rags

Nitrate salts placed on top of rags in Tests 11 and 20 underwent a temperature excursion that caused the lids and bottoms to bulge, but showed no evidence of an explosion. A scenario in which molten nitrates flowed into a punctured drum full of dried rags is unlikely, and if such a scenario did take place, would not lead to a violent reaction.

3.9   Explosion, Deflagration, and Detonation

The following definitions are taken from the *DOE Explosives Manual* (DOE 1996).

- **Explosive**: Any chemical compound or mechanical mixture that, when subjected to heat, impact, friction, shock, or other suitable initiation stimulus, undergoes a very rapid chemical change with the evolution of large volumes of highly heated gases that exert pressures in the surrounding medium. The term applies to materials that either detonate or deflagrate. DOE explosives may be dyed various colors, except pink, which is reserved for mock explosives.

- **Deflagration**: A rapid chemical reaction in which the output of heat is sufficient to enable the reaction to proceed and be accelerated without input of heat from another source. Deflagration is a surface phenomenon with the reaction products flowing away from the unreacted material along the surface at subsonic velocity. The effect of a true deflagration under confinement is an explosion. Confinement of the reaction increases pressure, rate of reaction, and temperature, and may cause transition into a detonation.

- **Detonation**: A violent chemical reaction within a chemical compound or mechanical mixture involving heat and pressure. A detonation is a reaction that proceeds through the reacted material toward the unreacted material at a supersonic velocity. The result of the chemical reaction is exertion of extremely high pressure on the surrounding medium, forming a propagating shock wave that is originally of supersonic velocity. When the material is located on or near the surface of the ground, a detonation is normally characterized by a crater.

More sophisticated definitions are often employed by detonation physicists, but for the immediate discussions, the above will suffice. It is clear that the energetic events experienced in this test series represent deflagrations and not detonations. The drums were deformed, the lids blown off, and the sound was heard, but nothing shattered. The reactions were explosions, but not the kind that shatters rocks and concrete or fragments steel. In only one case (Test 24) was a significant hole blown in the side of a drum.

4. CONCLUSIONS

A series of explosives tests (i.e., Henkins, Koenen, burn-rate, and 5- and 55-gal cook-off tests) demonstrated that $NaNO_3$ and KNO_3 salts could react explosively with rags, pyrolyzed rags, or graphite when subjected to a heating rate of 100°C per hour in a simulation of ISV thermal gradients. Mixing nitrate salts with the carbonaceous materials is not necessary for deflagration. Nitrate-soaked rags will also react explosively when similarly heated. Burn-rates of 2.4 to 23 cm (1 to 9 in.) per second can be achieved with the mixtures, confirming the possibility of fire propagation through mixed fuels and nitrates.

The explosions were deflagrations and not detonations. The explosions were initiated by heat applied to the drum walls by external heaters. Extrapolation can be made to the case of ISV melt contacting drums in the ground causing similar explosions.

These tests indicate that the effects of explosions can be effectively mitigated by a total of 3 m (10 ft) of dirt overburden. In the case of ISV, a pool of molten material will be in close proximity to the drum. The behavior of the hot explosion-product gases in possibly displacing, or rising through the melt, is not known. A full-scale test of nitrate and fuel drums under actual ISV conditions is recommended.

Many of the scenarios for contact and mixing are improbable. Because testing was performed with bounding conditions, effects greater than those observed in the tests are also improbable. The bounding conditions assume that only one drum of explosive mixture can be involved in any deflagration. Because of the limited number of tests, however, breaching the surface, even with 304 cm (10 ft) of overburden, cannot be positively excluded.

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